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AN UNUSUAL PENTADIENYL REARRANGEMENT: FORMATION OF A CYCLOPENTENYLCYCLOPENTENONE BY SOLVOLYSIS OF 1,3-DICHLORO-2,4-DIMETHYL-2,4-PENTADIENE

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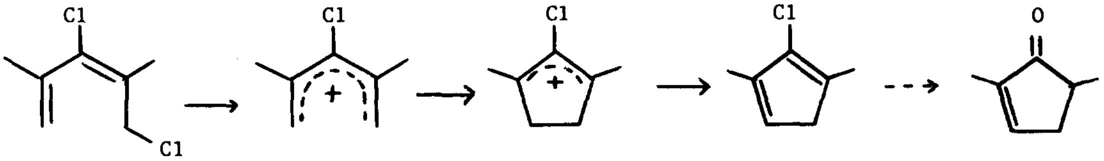
Pentadienyl cations are known to undergo a facile electrocyclic transformation leading to unsaturated five-membered cyclic products through cyclopentenyl cations.[1] Such cationic species have also been suggested as possible intermediates in the formation of cyclopentenones from the dichlorocarbene adducts of allylic alcohols.[2] It seemed likely then that dichlorides such as 1[3] could produce similar intermediates and that solvolysis of 1 in acidic conditions would yield 2,5-dimethyl-2-cyclopentenone, according to Scheme 1.



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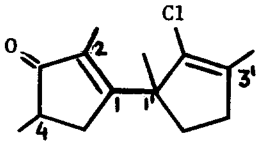
Scheme 1

Dichloride 1 was therefore subjected to a variety of acidic treatments, including warming in 48% hydrobromic acid,[2] but usually no unsaturated ketonic material could be detected. However, after heating under reflux in 80% acetic acid, 1 converted into one major ketonic product which was isolated, after chromatography and distillation, in 55-60% yield and shown to be the dimeric chloroketone 2.

Ketone 2 (b 160-165° (bath)/1 mm; red 2,4-DNP, mp 172-173°) was identified through its analytical and spectral properties: ν_{max} ($CHCl_3$) 1681 cm^{-1}; λ_{max} (EtOH) 238 nm (ε 14100); δ ($CDCl_3$) 1.15 d (J=7 Hz, 4-Me), 1.40 s (1'-Me), 1.72 t (J∼1.5 Hz, homoallylic splitting, 2-Me),



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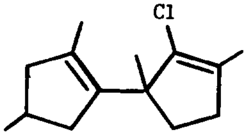

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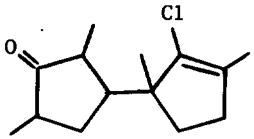

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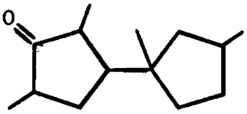

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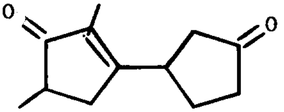

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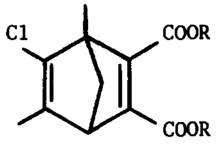
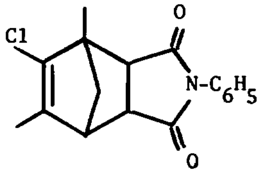
1.76 s (3'-Me), 1.7-3.15 m (7H). Mass spectrum: three most important peaks at m/e 238, 240 (M^+), 223, 225 (base peak) and 129, 131 ($C_7H_{10}Cl$, corresponding to the chlorine bearing moiety of 2). Anal: $C_{14}H_{19}ClO$ (C, H, Cl). The UV and ir spectra and the absence of a vinylic proton in the nmr indicated a cyclopentenone structure, with a fully substituted double bond. The mass spectral fragmentation of 2 and of its reduction products indicated the way in which the two moieties of the molecule could be bonded. Reduction of 2 over platinum in ethyl acetate produced a 1:1 mixture of compounds 3 and 4. The mass spectrum of 3 showed a molecular peak at m/e 224, 226 ($C_{14}H_{21}Cl$), a small peak at 209 and practically no fragment down to 129, 131 ($C_7H_{10}Cl$). The ir of 3 showed no carbonyl absorption. Ketone 4, $C_{14}H_{21}ClO$, ν_{max} 1733 cm^{-1}, showed in its mass spectrum peaks at m/e 240, 242 (M^+) and no fragments down to 129, 131 ($C_7H_{10}Cl$) and 111 ($C_7H_{11}O$, ketonic moiety of 4). Reduction of 2 over Pd/C in methanol, in the presence of MgO, yielded one product, ketone 5, $C_{14}H_{24}O$, λ_{max} 1732 cm^{-1}, m/e 208 (M^+), 123, 112, 97.

An important clue as to the structure of 2 was obtained from the reaction 1 with 2-cyclopentenone in boiling 80% acetic acid (1/2 hr). From this reaction was isolated in $\sim$ 10% yield the diketone 6, b 170-180° (bath)/1 mm; ν_{max} ($CHCl_3$) 1744 and 1690 cm^{-1} (two five-membered ring ketones, one saturated and one unsaturated); λ_{max} (EtOH) 238 nm (ε 15600); δ ($CDCl_3$) 1.20 d (methyl), 1.76 t ($J\sim1.5$ Hz, methyl, homoallylic splitting; these two signals are very similar to two out of the four methyl signals of 2), 1.8-3.8 m (9H); mass spectrum, m/e 192 (M^+), 177, 164, 150, 136, 121, 109.

Solvolysis of 1 in 80% acetic acid in the presence of dienophiles (acetylene dicarboxylic acid or ester, N-phenylmaleimide) gave in very good yields the adducts 7 to 9, with correct analytical and spectra properties.



7 R=H
8 R=CH_3



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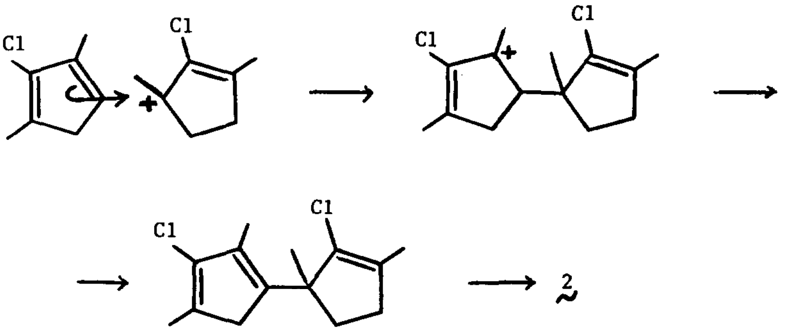
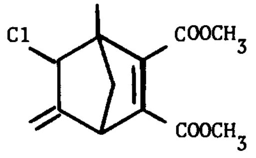
The formation of these adducts indicates that a chlorocyclopentadiene *is* formed during the solvolysis reaction of 1, probably as shown in Scheme 1. In the absence of a dienophile it combines with its methyl-stabilized cationic precursor and only the less hindered vinylic chlorine is then hydrolized to a ketone, yielding 2 (Scheme 2). Diketone 6 would be similarly formed by addition of the chlorocyclopentadiene to the protonated cyclopentenone.



Scheme 2

All attempts at the hydrolysis of the vinylic chlorine of 2, 3 or 4 have not succeeded until now. However, when adduct 8 is treated successively with sulfuric acid and then with water it yields a mixture of three compounds, obtained in varying proportions according to the temperature and duration of interaction with the sulfuric acid, in a total of 70-80%. These are the isomerization product 10, the hydrolysis product 11 (one isomer, mp 47-48°) and the chlorohydrin 12 (one isomer, mp 129-130°). Further treatment of 10 with sulfuric acid in the reaction



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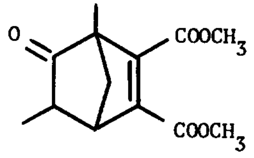

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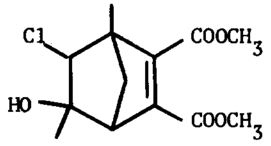

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conditions converts it almost totally into the chlorohydrin 12.

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3. Y. Gaoni, *Tetrahedron Letters*, 2167-2170 (1976).